

1915
R82

RUBY

The Fusibility of Coal Ash

Chemical Engineering

B. S.

1915

THE UNIVERSITY
OF ILLINOIS
LIBRARY

1915
R82



THE FUSIBILITY OF COAL ASH

BY

GEORGE BENJAMIN RUBY

THESIS

FOR THE

DEGREE OF BACHELOR OF SCIENCE

IN

CHEMICAL ENGINEERING

COLLEGE OF LIBERAL ARTS AND SCIENCES

UNIVERSITY OF ILLINOIS

1915



Digitized by the Internet Archive
in 2013

<http://archive.org/details/fusibilityofcoal00ruby>

1915
F82

UNIVERSITY OF ILLINOIS

May 25, 1915

THIS IS TO CERTIFY THAT THE THESIS PREPARED UNDER MY SUPERVISION BY

George Benjamin Ruby

ENTITLED THE FUSIBILITY OF COAL ASH

IS APPROVED BY ME AS FULFILLING THIS PART OF THE REQUIREMENTS FOR THE

DEGREE OF BACHELOR OF SCIENCE IN CHEMICAL ENGINEERING

H. J. Broderson.

Instructor in Charge

APPROVED:

W. A. Woyne

HEAD OF DEPARTMENT OF

Chemistry

1015
R82

TABLE OF CONTENTS.

	<u>Page.</u>
I. Introduction,	1
II. Historical,	2
III. Experimental,	6
A. Analysis,	6
B. Apparatus,	11
C. Fusibility Determination,	14
IV. Results,	14
V. Summary,	16

- - - - -

- - - - -

THE FUSIBILITY OF COAL ASH.

- - - - -

Introduction.

The ashes of different coals have widely varying fusing temperatures, as they also have widely varying chemical compositions. The object of this investigation is to try to find a relation between these two characteristics of coal ash. The justification of the work lies in the fact that a determination of the fusing point of a coal ash is of value to buyers, for a low melting ash entails additional expense in many operations involving the combustion of coal. Since this problem involves a chemical analysis and a fusion of the ash to find where it becomes fluid, two divisions have been made, the first, the chemical analysis, the second, the determination of the fusion point of the ash.

Historical.

All data on this problem has been accumulated within the last few years by a number of independent workers, who, however, often arrived at very different conclusions using the same results.

Dr. E. J. Constan (✓) reports as a result of his work

✓ Journal Gas Lighting, Vol. 124, p.522.

the following: - The percentage of ash in a coal has no influence on the fusing temperature of the ash; the fusing temperature is a characteristic of the coal seam; finally, the fusing temperature of an ash may not depend entirely on the percentage of a compound present, but depends partly on the distribution thereof. He states that various impurities in coal such as slate may influence the fusing temperature of the ash. The presence of lime, iron, and pyritic sulphur tends to lower the melting point, but alumina tends to raise the melting point.

O. W. Palmenburg (✓) analyzed about thirty ashes and

✓ Journal Industrial and Engineering Chemistry, April 1914.

states "that the sulphur content of the coal has no bearing whatsoever upon the fusibility of the ash;" "that there is no

relation between the percentages of the various constituents of the ash and the fusing temperature"; and that "therefore, a chemical analysis is of no value to arrive at a conclusion regarding the clinkering quality of a coal". In the same article Mr. Palmenburg states "that to get the value of a coal for steaming purposes, it is therefore just as essential to make the fusing temperature test of the ash as it is to make the calorimetric determination." In answer to this article, and by using the same data, J. H. K. Burgwin (*) states that an ash con-

* Journal Industrial and Engineering Chemistry, August 1914.

taining less than 10 percent of iron does not fuse at a temperature lower than 2550° F. (= 1400° C.), and that when the iron content exceeds 20 per cent the fusing temperature is never higher than 2550° F. With the same data Mr. Burgiven also plotted the fusing temperature against the sum of the sulphur and the iron of the coal, which showed clearly that under 3 percent of sulphur plus iron the fusing temperature of the ash is above 2550° F. and over 3 percent it is below that point.

W. H. Fulweiler (*) gives some analyses of coal ash and

* Rogers and Aubert Manual of Industrial Chemistry, 2nd Edition, p.439.

their melting points, but he gives no discussion of any relation between the two.

In an article in the United States' Geological Survey, L. P. Breckenridge (✓) recommends an investigation of the

✓ U. S. Geological Survey, 557 x B 325 p.35.

relation of the fusibility of coal ash to its composition in the following ways: - Ash analysis, experimental determination of the melting point, and a determination of the manner of distribution in the coal of the various constituents of the ash. Mr. Breckenridge, from data on 300 coals, states that iron may not cause clinkers but the two are usually found together; that high iron and low ash percentages give a low melting point; that clinkering is bad if the Fe S₂ percentage is high and the ash percentage is low; that clinkering usually varies directly as the sulphur content and inversely as the ash percent, but that no variation occurs using different sizes of coal.

In a report(✓) read before a body of coal users in New

✓ Report of a Committee on Steam Operation read before the 30th Annual Convention of the Association of Edison Illuminating Companies. Sept. 15, 16, 17, 1914.

York, melting points, but no chemical examinations were made of a number of coal ashes. The conclusions were that coals having ashes of a melting point above 2500° F. are non-clinkering for ordinary steam purposes, and that those whose ashes melt below 2400°F. are clinkering.

L. S. Marks (✓) summarized the present situation in a

✓ L. S. Marks, Harvard University, "The Clinkering of Coal".

very thorough manner and gave valuable instructions as to the determination of the fusing point of a coal ash. The method used by Mr. Marks has been generally followed in this investigation.

A. C. Fieldner (✓) and A. E. Hall have given a review

✓ Journal of Ind. & Eng. Chem. May 1915.

of the different results obtained in determining the fusion point by using various atmospheres. They find there is a great difference in different atmospheres, but have drawn no conclusions as yet.

Experimental.

Analysis. - An analysis of a coal ash should include the following elements: - Si, Fe, Al, Ca, Mg, and S. There are others present such as Ti, K, and Na, but ordinarily these are present in such small amounts that they may be neglected.

The sample of clinker or coal ash is ground to pass 100 mesh sieve and is then thoroughly mixed. A 3 gram sample is as large as can be easily manipulated. This is fused for fifteen minutes with 5 grams of Na_2CO_3 in a covered platinum crucible. By lowering the red hot crucible into cool water but not allowing the water to get inside, the fusion may be loosened from the crucible. When cool, dry and clean the outside of the crucible carefully, and place it and the cover in 150 cc. of distilled water; add 20 cc. conc. H Cl and heat to boiling on an iron plate. When the fusion is in solution, wash and remove the crucible and cover, and evaporate the whole on the water bath. Now place the container in an oven and heat to about 180°C . for a half hour, which process dehydrates most of the silicic acid. Add 100 cc. water and 20 cc. conc. H Cl and heat on the water bath until nothing but Si O_2 remains as a residue. Filter through a quantitative filter paper and evaporate the solution as mentioned above. Heat again to 180°C . and bring into solution as before to remove the remaining silicic acid. Filter, and if the second drying

produces much Si O_2 repeat the process, and ignite the two or more precipitates in the platinum crucible.

The ignited residue is weighed, but since it is not all Si O_2 , but contains some iron, about 5 cc. conc. H_2SO_4 and 1 or 2 cc. of H F solution are added, and then the crucible is heated to remove the H_2SO_4 , H F, Si F_4 and H_2O . A convenient method of evaporating these was found to be by placing a false bottom of asbestos in a three inch iron crucible, leaving about an inch between the bottoms. This gave even heating and also allowed three samples to dry at once. The iron crucible should be placed in a hood to remove the fumes. When the crucible is dry, heat to redness to destroy the sulphates of iron formed, and weigh again. The loss in weight is Si O_2 , the residue being iron oxide and can later be combined with the iron precipitate of the sample.

The filtrate from the last drying of the sample is now heated to boiling and treated with 5 cc. bromine water to oxidize the iron. The solution should be boiled for ten minutes to remove excess bromine. Neutralize, and make slightly alkaline with ammonia; then boil again for ten minutes to remove all excess ammonia, for although ammonia precipitates iron and aluminum as the hydroxides, any excess will dissolve some Al (OH)_3 . Filter on to quantitative paper, wash once or twice, and dissolve the precipitate in hot dilute H Cl. Re-precipitate in 100 - 150 cc. of water using the same precautions as before and pour through the same filter. Wash

twice, combine the filtrates and save. This precipitate should be ignited, preferably in platinum, weighed as Fe_2O_3 and Al_2O_3 , and brought back into solution with fused KHSO_4 . About fifteen times the weight of precipitate is taken of the KHSO_4 , and mixed with the precipitate. The crucible is covered, heated gently at first, and then heated to redness until the SO_3 fumes have nearly ceased and there are no more specks in the fusion. The crucible can be cooled just as in the first fusion but instead of using HCl , the mass in the crucible is dissolved by using hot water only. When the fusion has dissolved remove the platinum ware and examine the solution. If heavy black specks are found the fusion was incomplete and it may be necessary to filter and repeat the fusion, but if the solution is clear, the iron may be reduced either with SnCl_2 and HgCl_2 , or by the Jones reductor, the latter method having been used in this work. In order to secure the best results with a Jones reductor, the iron solution should be hot and run through slowly. Titrate the reduced solution at once with standard KMnO_4 to find the amount of iron present, and subtract from the result, the result of a blank run on the Jones reductor for iron. By the titration the amount of iron present may be found and the amount of Al_2O_3 can be obtained by difference.

To the filtrate from above, unless a large amount of ammonium salts is present, is added 25 cc. saturated NH_4Cl solution. The resulting solution which should be slightly alkaline with ammonia is brought to boiling and 10 cc. of

$(\text{N H}_4)_2 \text{ C}_2\text{O}_4$ (40 grams per liter) are added slowly with stirring. Stir well and then let the whole stand for at least an hour. Filter, blast the precipitate for half an hour and weigh as CaO .

The filtrate from the calcium precipitation is evaporated on the steam bath until the salts just begin to crystallize and then just enough water is added to dissolve them. To this concentrated solution 10 cc. $\text{NaH} (\text{N H}_4) \text{ PO}_4$ (100 grams per liter) are added slowly with stirring. After the $\text{Mg} (\text{N H}_4) \text{ P O}_4$ has started to precipitate, a volume of dilute NH_4OH equal to one-third of the solution, is added and the whole is allowed to stand 24 hours. This precipitate is then filtered and is ignited slowly. When the carbon is burned the precipitate is blasted for about two hours. If on thorough ignition the carbon is not removed, add a drop or two of conc. H N O_3 and ignite. Calculate as $\text{Mg}_2\text{P}_2\text{O}_7$.

For sulphur determinations, a sodium peroxide cup devised by Professor S. W. Parr was used, the charge being given below.

1 gram Coal Ash

1/2 gram Benzoic acid

1 measure Na_2O_2

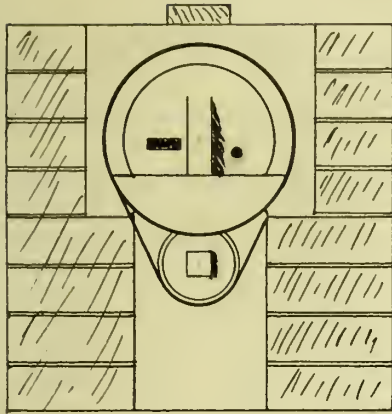
The fusion is dissolved in pure water and after washing and removing the cup, H Cl is added until an acid reaction is reached. The solution is now boiled, filtered to remove any impurities, and the sulphate precipitated with Ba Cl_2 in the

The precipitate is allowed to stand an hour, when it is filtered and weighed as BaSO_4 .

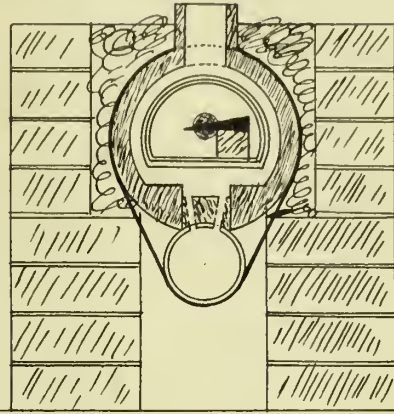
Some ashes contain carbon which should be determined by igniting in a flat dish a sample of the ground ash and finding the loss in weight. It must be remembered, however, that unless the ash is fresh, the lime may have absorbed some CO_2 and besides some S may have been oxidized.

Diagram of the Fusion Furnace.

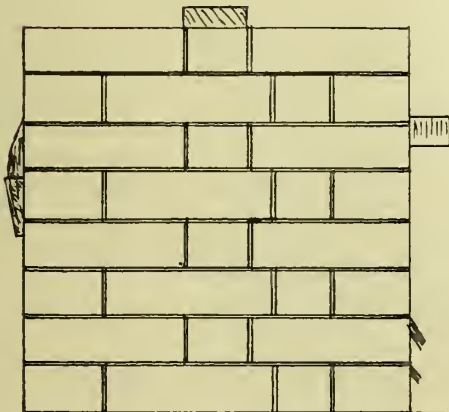
G. B. Ruby.



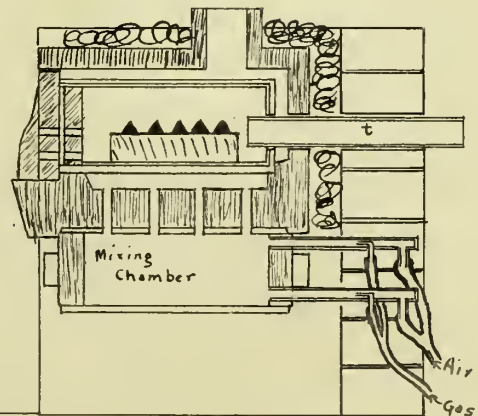
Front View.



Vertical Cross-section.



Side View.



Horizontal Cross-section.

LIBRARY
OF THE
UNIVERSITY OF ILLINOIS.

Fusion of the Ash. - A furnace suitable for high temperatures, a pyrometer which can be used from 1000°C. to 1700°C., and a cone mold are necessary in determining the fusion temperature of a coal ash. In this work a Wanner pyrometer, using a current from two lead cells in series, was used. The instrument was standardized at each fusion against the amylacetate lamp. The manner of getting the temperature was by directing the pyrometer tube towards the ash cones through the tube (t). The temperature of the cones could be followed closely by this means and the fusion temperature could be obtained quite accurately.

Since coal ash has no exact melting point a method has been used to obtain the range of melting as nearly as possible. The method has been to make a Seger cone of the ash ground to pass 100 mesh using a ten percent glucose solution as a binding liquid, and to melt this in the furnace. Seger cones of definite size, 52 mm. in height, were made in the cone mold which was moistened with kerosene to facilitate removing the cone after formation. The cone was removed from the mold and placed on an iron plate where it was heated until it baked into a hard mass, but was not fused. Three to five cones were made of each ash to serve as checks.

The furnace was the most difficult part of the apparatus to obtain. After it had been decided to use gas as a fuel, several types of furnaces and muffles were tried. The first furnace which was tried was built of a large Denver fire clay

crucible placed vertically with flame entering horizontally at the bottom. This furnace was inadequate for it was so made that temperature readings were quite impossible and an observation of the ash cone was totally out of the question. Therefore, another furnace was built which had a horizontal muffle 4 inches wide, $3\frac{1}{2}$ inches high and 8 inches deep. Around the outer jacket a brick support was built, leaving room for about 2 inches of asbestos packing on all sides between it and the outer furnace jacket. When the furnace was assembled, but two openings remained in the outer jacket, one above for escaping gases, and one below for the admission of gas. The upper opening was merely a chimney of $1\frac{3}{4}$ inches internal diameter, while the lower opening was 6 x 2 inches and extended beneath the whole muffle. At first a water cooled blast lamp was arranged to direct its flame against the bottom of the muffle thru a sand-lime brick. The brick, however, cracked and then a graphite cylinder was substituted. The graphite, being heavy, lasted some time, but it gradually burned out. By these means a high enough temperature was obtained, but since a permanent furnace was needed, a different type of burner, having about four times the former tuyser area was made. This change cut down the speed of the gases and provided a more uniform heating. The new burner has eight $\frac{3}{8}$ inch tuyers, as is shown in the drawing. The tuyers were made of alundum mixture, 85 per cent fused Al_2O_3 and 15 per cent Tennessee ball clay. The mixing

chamber for the gases is made of iron pipe closed at both ends with eight $3/8$ inch holes on top feeding into the tuyers. It in turn receives gas from two blast burners, which allow the air to suck in all the coal gas needed for combustion. A large iron pipe has been introduced into the air system to allow the water in the air blast to settle and be removed. With this arrangement a temperature of about 1750° C. was obtained, but on examination of the furnace on cooling, it was found that the Denver fire clay muffle had melted and collapsed.

A new alundum muffle was ordered, but is not yet installed and in the meantime a new Denver fire clay muffle was lined with some alundum mixture ground to pass about an 8 mesh sieve. The new muffle so lined has held its shape well and seems to be quite satisfactory. An inner door of the same mixture has been made to fit inside the fire clay muffle as the drawing shows. With the present arrangement very good results can be obtained, but if a strongly oxidizing flame of low temperature is desired for some time it would be well to tap and plug two of the tuyer holes in the iron cylinder. The burner when turned low at present and given considerable excess of air may "strike back", when the iron chamber which is usually cool gets very hot. Striking back may be remedied by giving more gas or more gas and air together. An air hole has been provided in both doors so that air may be blown into the muffle to insure plenty of oxygen to give an oxidizing atmosphere.

Method of making a Fusion. - Having made Seger cones of the ash according to directions given above, from 3 to 5 cones were placed in the muffle in full view of the pyrometer through the sight tube. The gas was then turned on, and lighted at the chimney. Air was then admitted until the proper flame was obtained. A flame was used which heated the furnace gradually, about twenty minutes usually being taken to get it up to full heat. Air can be admitted through the air holes in the doors to keep the muffle well supplied with oxygen. When the temperature is about 1000° C. the rate of increase should be decreased, observing the cones and following their temperature with the pyrometer. When the point begins to vitrify, reduce the rise to 2° C. per minute and find the temperature interval from where the cone starts to bend and the temperature when its point touches the alundum block.

RESULTS.

<u>Coal.</u>	<u>I.</u>	<u>II.</u>	<u>III.</u>
Carbon,	1.63%	--	---
Si O ₂	43.37%	46.40%	45.16%
Fe ₂ O ₃	24.40%	24.70%	28.30%
Al ₂ O ₃	12.62%	19.00%	17.80%
Ca O	14.00%	9.50%	7.80%
Mg O	4.12%	2.00%	trace
S	5.45%	none	4.82%
Melting Point	<u>I.</u> 1090°-1170°	<u>II.</u> 1145°-1172°	<u>III.</u> 1097°-1120°.

Coal I - Peoria screenings 1914.

Coal II - Clinker removed from boiler smoke chamber.

Coal III - Clinker from an Illinois Coal.

SUMMARY.

As will be seen by looking over the results above, not enough ashes have been investigated to draw conclusions, but it will be noted that all three have a low fusion temperature; that two have high sulfur and the other has high lime contents; that the one having no sulfur melted above the other two; and that in all cases the results corroborated the conclusions given by Mr. Burgwin, which were that ashes which contain more than 20 percent of iron never fuse higher than $2550^{\circ}\text{ F. (=1400}^{\circ}\text{C)}$.

Some investigators have determined fusion points for both oxidizing and reducing temperatures, and although the relation of these to each other may be valuable, still it would seem that burning coal in the region of clinker or ash formation would invariably have one atmosphere. It would seem that such an atmosphere would be oxidizing, and if so, the oxidizing furnace atmosphere should be used in getting the fusion temperature of the ash.

The work done has suggested that it might be of considerable importance in the solution of this problem if a thorough trial were made of empirical ashes. Such mixtures might be made duplicating some analyzed ashes, and comparative fusions of these could then be made. If it were possible to get analogous fusion temperatures, the problem could probably be partly solved by this means.

Furthermore additional information might possibly be obtained if a microstudy of the clinker or fused ashes were made. The more fluid portions might give evidence of what tends to produce a clinker.

- - - - -

References:

Talbots Quantitative Analysis.

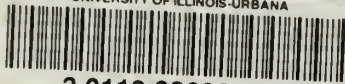
Treadwell & Halls Analytical Chemistry, Vol. II.

- - - - -





UNIVERSITY OF ILLINOIS-URBANA



3 0112 086831127